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博 士 学 位 论 文

从头算价键理论方法研究

A Study on Ab Initio Valence Bond Method

陈振华

指导教师姓名：吴　玮　教　授
专　业　名　称：物　理　化　学
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摘　要

作为最重要的化学键理论之一，价键理论曾经风靡整个化学界。后来由于价键理论中非正交轨道造成的计算困难和分子轨道从头算方法的发展，使得后者的应用越来越广泛，逐渐成为目前理论化学计算的主流方法。在许多化学工作者的努力之下，从上世纪八十年代开始，价键理论正在经历缓慢的复兴。本文尝试在价键理论框架下发展新算法以提高原有的价键方法的计算效率；发展新方法以提高价键理论的计算精度和推广价键理论的应用范围等方面作一些工作。下面是各章的安排。

在第一章中，我们介绍了张量分析的一些基本知识。

在第二章中，使用张量知识我们定义了非正交轨道的产生和湮灭算符，并使用它们发展了非正交轨道下的二次量子化方法。为后面章节公式的推导提供了一个有用的数学工具。

在第三章中，通过引进一组与非活性轨道正交的辅助活性轨道和相互正交且正交于占据轨道的虚轨道简化了价键能量，梯度和 Hessian 的计算。通过小心的设计价键行列式矩阵元计算的程序，我们完全避免了计算不必要的重复计算并且不用存储行列式矩阵元。通过将非活性轨道按基函数展开，计算能量和梯度时双电子积分变换只需对活性轨道进行。使用非正交轨道的二次量子化方法，我们大大的简化了公式的推导过程并将价键能量，梯度和 Hessian 用密度矩阵表示了出来。基于这些公式，我们设计了有效的 VBSCF 优化算法。测试的计算表明新的算法比现有的其它优化方法要快很多。

在第四章中，我们发展了价键二级微扰理论方法(VBPT2)。计算表明，该后价键自洽场方法具有计算量小和精度接近其它复杂的价键或分子轨道方法的特点。VBPT2 方法由 VBSCF 计算使用的很少的价键结构集出发，通过 VBSCF 计算的密度矩阵引入了广义的 Fock 矩阵，然后构造了 Møller-Plesset (MP) 类型的零级 Hamiltonian。VBPT2 的一级校正波函数展开为单双激发价键结构的线性组合。这些激发价键结构中的虚轨道正交于占据轨道。通过将激发结构对波函数的贡献收缩到基本的 VBSCF 结构中，VBPT2 的波函数可以像 VBSCF 那样易于理

解。使用 VBPT2 方法，我们测试了 H_2，F_2，N_2，O_2 等分子的键能，等同氢提取反应的反应能垒，水分子的对称解离势能面和 F_2 分子中共价结构和离子结构的权重和它们的共振能。计算表明 VBPT2 的结果与 VBCI 和分子轨道理论中的 MRPT 和 MRCI 方法的结果一致。而与 VBCI 方法相比，VBPT2 的计算量要小很多。对 VBPT2 方法我们还发展了激发空间的收缩技术，使用该技术我们能够进一步减小 VBPT2 方法的计算量。

在第五章中，我们提出了收缩的直接矩阵元的价键组态相互作用方法，该方法在 VBSCF 方法的基础上进行 CI 计算以引进动态相关能。使用相互正交且正交于占据轨道的虚轨道和激发空间的收缩技术，我们简化了 VBCI 方法中矩阵元的计算公式。我们还发展了直接矩阵元技术并将分子轨道 CI 方法中 CI 波函数的优化方法推广到了非正交的情形，使得我们能够容易的处理组态数非常多的 VBCI 波函数。本文的方法克服了 VBCI 方法中价键结构很多时，矩阵元无法存储和久期方程无法求解的困难。大大的推广了 VBCI 方法的应用范围。而且上述的直接矩阵元方法也能够应用于 VBSCF 的计算。

在第六章中，我们发展了基于 Lewis 结构的价键计算方法(LVB)。该方法使用由半定域的键轨道和定域的杂化原子轨道构造的双占据 Slater 行列式来描述 Lewis 结构。根据替换不同数目的键轨道为杂化原子轨道，LVB 方法的级别有 LVBS，LVBSD 等。LVBS 表示只替换一对键轨道为相应杂化原子轨道；LVBSD 则替换两对键轨道为杂化原子轨道，依此类推。测试计算的甲烷，亚甲基烯和笨等三个例子表明了 LVB 方法的计算结果与 VBSCF 方法的很一致，虽然 LVB 波函数中所用的行列式很少。该方法对价键轨道较多的情形能够容易的处理，扩大了价键方法的应用范围。

在第七章中，使用价键方法和电荷密度分析方法，我们对一系列 C-C 键的本质进行了研究。十六个 C-C 键化合物的价键计算和电子密度分析表明了这些 C-C 键分成了两类。第一类包含了乙烷，环丙烷等。其中 C-C 键是共价键既共价的自旋配对方式对键能的贡献起了主要作用。第二类包括了螺浆烷类小环化合物中的桥键，该键既不是由共价结构也不是由离子结构使之稳定的，而是这两者之间的共振。因此称之为电荷移动（CS）键。这两类 C-C 键也可以从实验或计算的电子密度中看出来。共价键的电子密度特征是在键临界点处密度的 Laplacian 是

负的，而 CS 键的却是很小或正的 Laplacian。正的 Laplacian 表明了键临界点(BCP)附近的作用方式是排斥相互作用，这也是反向 C-C 键中的情形。这样的区域一般动能较大，电子密度分析的结果的确得到了这个结论。大的共价与离子结构的共振能有利于成键区域动能降低进而使分子能够保持平衡键长。因此，不同的排斥张力产生了两类不同 C-C 键。进一步分析表明排斥张力能够解释不同大小和不同取代基的螺浆烷的性质差异。实验结果表明螺浆烷中的 C-C 键能够很好地分成两类，其中反向的 C-C 键是 CS 键而翼上的 C-C 键是共价键。CS 键还有什么其它表现吗？实验上的回答为重绘化学键的图景提供了一种可能性。

关键词：价键理论；自洽场方法；微扰方法；组态相互作用方法；螺桨烷

Abstract

As one of the most important chemical bond theories, valence bond (VB) theory has been very popular in chemistry. Due to the computational difficulty of non-orthogonal orbitals and the development of molecular orbital theory, Molecular orbital (MO) theory became more and more popular and gradually makes itself as the mainstream method in computational chemistry. Starting from the 1980s and onwards, VB theory has been enjoying renaissance by the development of ab initio computational methods. In this thesis, we are trying to develop new algorithms for VB methods to improve their performance, to develop new computational methods for accurate VB calculations, and to extend the VB applications. The thesis is organized as follows:

In Chapter 1, the background of tensor is introduced.

In Chapter 2, the creation and annihilation operators in the second quantization method is extended to VB theory, wherein non-orthogonal orbitals are used. The form of the second quantization VB theory provides a powerful mathematical tool for the development in the computational VB method that shall be discussed in the later chapters.

In Chapter 3, an efficient algorithm for the optimization of VBSCF wave function is developed. The computaional costs of VB energy, gradients, and Hessians have been greatly reduced by introducing the auxiliary active orbitals, which are orthogonal to the orthogonalized inactive and virtual orbitals. By designing the code very carefully, the repleated evaluations of the matrix elements between two determinants are completely avoided in the new algorithm and the matrix is not required to store. By expanding the inactive orbtals in terms of basis functions, the integral transformation is required only for the active orbitals. Using the non-orthogonal orbital based second quantization method, we express all requisite formulae in terms of density, such as energy, gradients and Hessians. Test calculations show that the new

algorithm is much faster than the old ones in the XMVB package.

In Chapter 4, a post-VBSCF method, called valence bond second-order perturbation theory (VBPT2), is developed in this paper and is shown to be (i) economical, and (ii) at par with more sophisticated VB and MO-based methods. The VBPT2 method starts with VBSCF using a minimal structure-set. Subsequently, the Møller-Plesset (MP) partition of the zeroth-order Hamiltonian is obtained by introducing a generalized Fock matrix constructed from the VBSCF density matrix. The first-order wave function is expressed in terms of singly and doubly excited VB structures, which are generated by replacing occupied orbitals by virtual orbitals; the latter being defined as orthogonal to the occupied orbitals. The VBPT2 method retains the simplicity of a VB presentation by condensing contributions from the excited structures into the minimal number of fundamental structures that are involved in the VBSCF calculation. The method is tested by calculating the bond energies of H_2, F_2, N_2, O_2, the barriers of identity hydrogen abstraction reactions, the atomization energy and a potential energy curve for the water molecule and the structural weights and covalent-ionic resonance energy of F_2. It is shown that the VBPT2 method gives results in good agreement with those of the VBCI method and molecular-orbital based methods such as MRPT and MRCI at the same truncation levels. However, the computational effort is greatly reduced, compared to that of VBCI. Future potential directions for the development of the VBPT2 method are outlined.

In Chapter 5, an improved valence bond configuration interaction is developed by using coefficient contraction technique, thus called contracted VBCI (CVBCI). In this method, the evaluation of the matrix elements in VBCI is simplified by contracting the exited space and by using the orthogonal constraint of the inactive and virtual orbitals. The direct algorithm for the MO-based CI is extended to the nonorthogonal VBCI method, and thus the secular equation of the VBCI wave function with numerous VB structures can be easily solved, extending the VBCI applications to larger molecule systems. Moreover, the direct matrix element algorithm is able to apply to the VBSCF method.

In Chapter 6, a valence bond method based on Lewis structures, called LVB, is presented. The method uses a Slater determinant expansion of doubly occupied orbitals for describing a Lewis structure, where two orbital sets, semi-localized orbitals, called bond orbitals, and hybrid localized orbitals (HAOs), are employed. The levels of LVB method are fashioned as LVBS and LVBSD etc. LVBS involves only the single bond orbital replacements with HAOs, while LVBSD involves also double replacements, and so on. Tests of three examples, methane, methylene, and benzene, show that the LVB method at both of LVBS and LVBSD levels gives results that match those of the VBSCF method very well, even though the form of LVB wave function is much compact.

In Chapter 7, VB method and electron topology analysis are applied to study the nature of C-C bonds. Valence bond and electron density computations of 16 C-C bonds show two families of bonds that flesh-out as a phase diagram. One family, involving ethane, cyclopropane etc., is typified by covalent C-C bonding wherein covalent spin-pairing accounts for most of the bond-energy. The second family includes the inverted bridgehead bonds of small propellanes, where the bond is neither covalent nor ionic, but owes its existence to the resonance stabilization between the respective structures; hence a charge-shift (CS) bond. The dual-family emerges also from calculated and experimental electron density properties: Covalent C-C bonds are characterized by negative Laplacians of the density, whereas CS-bonds display small or positive Laplacians. The positive Laplacian defines a region suffering from neighbouring repulsive interactions, precisely the case in the inverted bonding region. Such regions are kinetic-energy rich, and indeed the energy-density analysis reveals that CS-bonds are kinetic-energy-richer than the covalent C-C bonds. The large covalent-ionic resonance energy is precisely the mechanism that lowers the kinetic energy in the bonding region and restores equilibrium bonding. Thus, different degrees of repulsive strain create two bonding-families of the same chemical bond made from a single atomic constituent. It is further shown that the idea of repulsive strain is portable and can predict the properties of propellanes of various sizes and different wing substituents. Experimentally, the C-C bond families are beautifully

manifested in [1.1.1]propellane where the inverted C-C is a CS-bond, while the wings are made from covalent C-C bonds. What other manifestations can we expect from CS-bonds? Answers from experiment have the potential of re-charting the mental map of chemical bonding.

Keyword: Valence Bond theory; Self-Consistent Field Method; Perturbation Theory; Configuration Interaction; Propellane.